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STUDY ON DEASPHALTING AND DEMETALATION OF HEAVY PETROLEUM RESIDUE: PART II

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ABSTRACT

The role of dispersed catalyst in hydroconversion of heavy vacuum residue is to suppress the cause formation and promate the upgrading reaction sulfur, nitrogen, metals removal and conradson carbon reduction. In this study, the effect of temperature (350 - 425°C) and catalyst/ feed ratio (1/10, 2/10 and 3/10) on the hydrodemetallation (HDM), hydrodesulphurization (HDS), conradson carbon removal and product distribution of heavy vacuum residue has been investigated. Three spent catalyst are used which produced from different refining processes. Comparison between the yield and performance of the product by using the three spent catalysts at 400°C and catalyst/feed ratio 2/10 shows that HDS, HDM and conradson carbon removal for spent catalyst produced from hydrodesulphurization of kerosene was higher than that of spent catalyst produced from hydrodesulphurization of gas oil and spent catalyst produced from rerefining of waste lube oil.

INTRODUCTION

The use of dispersed catalysts may offer an interesting solution to upgrading heavy feed stocks and petroleum residues. In fact, the slurry processes combine the advantages of the carbon rejection technologies in terms of flexibility with high performances peculiar of the hydrogen addition processes [1 - 4].

Very high levels of catalyst dispersion, which strongly effect the hydrogen uptake, can be achieved by introducing finely divided powders or water or oil-soluble compounds into feed. The active species of the catalyst is a metal sulfide, which is generated in situs by thermal decomposition of the precursor [5].

In the last few years, many aspects dealing with the use of dispersed catalyst have been explored rather extensively; nevertheless, the problems associated with the development of slurry processes are not completely solved [6]. Main limitation to their commercialization concern the high investment and operating costs due to the catalyst make-up /or the severity of the process. At present, the most advanced slurry technologies [7 – 10] are based on the use of inexpensive, additives, for instance Fe- based compounds or carbonaceous material to control coke formation. The role of dispersed catalyst in hydro processing of heavy vacuum residue is to suppress the coke formation and promote the upgrading reaction (sulfur, metals removal and conradson carbon reduction [11]. In the present work we used inexpensive spent catalyst for upgrading the heavy residue. In order to produce deasphalted. In order to produce deasphalted oil,such deasphalted oil may be economically used in a catalytic- cracking process.

Experimental work

Feedstock: The vacuum petroleum residue was obtained from Suez Petroleum Co(12) and have the characteristics show in part(1)

Catalyst: Three spent catalysts in the crushed form were used

Spent catalyst (1) produced from hydrodesulphurization of kerosene (used for ten years)

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Spent catalyst (2) produced from hydrodesulphurization of gas oil(used for ten years)
Spent catalyst (3) produced from re- refining of waste lube oil (used for five years)
The characteristics of the three spent catalysts are indicated in table (2).

Catalyst pretreatment. The catalyst contaminants, such as residual oil, sulfur and coke were removed as follows:-

1- Washing the spent catalyst first with naphtha and then with toluene in a soxhlet extraction reactor in order to remove residual oil.

2- The clean catalyst containing coke, sulfur and metals was then, dried in an oven at 120°C for two hrs. The dried catalyst was subjected to carbon disulfide (100ml/10gm) with agitation at room temperature in closed flask for 12 hrs and then the product was filtered and dried in air at room temperature followed by heating in an electric oven to 450°C at 25°C/h maintained constant for 20 hrs in order to remove both carbon (decoked) and the remaining sulfur.

Experimental procedure and analysis:-

The reaction was conducted in a stainless high-pressure autoclave reactor (Parr-Model 4572), magnetically stirred, with an inner volume of 1800 ml and heated by digital controller. Reaction conditions were as follows:- reaction temperature 375-425°C, initial hydrogen pressure 60 bar, process time two hrs, and catalyst to feed ratio; 1/10, 2/10, 3/10 (wt/wt). At the end of the reaction the autoclave was left to cool to room temperature, untill total pressure decreased. The gas product was collected and the liquid product was filtered to separate solid catalyst, then analyzed according to ASTM standard methods to obtain the distillation curves of volatile fractions.

RESULTS AND DISCUSSION

1- Effect of Reaction Temperature:-

Table (1) represent the characteristics of the catalyst used the effect of reaction temperature during hydroprocessing of vacuum residue on the product distribution and the performance of the product of the three spent catalyst was studied in the range of 375-425°C. Experimental results for hydrodesulphurization, hydrodemetallation and conradson carbon residue of three spent catalyst as a function of temperature are presented in Table (2 - 4), and Figures.(1 and 2). It is clear that generally the product quality was improved when reaction temperature was increased, while the heavy oil > 500°C was decreased. This is attributed to the powder catalysts act as a site for deposition of metals and coke [2] and the feed oil fraction of hydrocarbons were converted to lower carbon number hydrocarbons.

2- Effect of catalyst/ feed ratio

Tables (5 - 7) and Figures. (3 and 4) represent the effect of catalyst to feed ratio on the quality and distributions of the product. It is seen that by increasing cat/feed ratio the quality of the product are improved and at the same time heavy oil > 500°C yield is decreased due to the increase dispersion of the catalyst with feed and due to increase the active metals of the catalyst (Co, Ni, Mo) and then the catalytic activity increase.

Tables (8 and 9) shows that the comparison between the yield and performance of the product by using the three spent catalysts at 400°C and catalyst/feed ratio 2/10. It can be concluded that the hydrodemetallation (HDM) activities for the three spent catalysts were higher than that for the hydrodesulphurization (HDS) activities. It shows that hydrodesulphurization (HDS), hydrodemetallation (HDM) and conradson carbon removal for spent catalyst (1) was higher than that of spent catalyst (2) and spent catalyst (3). This is due

to that the spent catalyst (1), which produce from HDS of kerosene having high surface area and average pore diameter than that of the other catalysts.

Table (1): Characteristics of spent catalysts

Characteristics / catalyst	Spent (1)	Spent (2)	Spent (3)
Chemical composition wt%			
Mo	12.7	10.5	9.79
Co	2.9	2.1	---
Ni	---	---	2.68
Al	35.7	33.9	32.81
Physical characteristics			
Surface area, m2/g	79	6 8	60.9
Average pore diameter, A°	645	423	229.4

Table (2): Effect of Reaction temperature on hydroprocessing of vacuum Residue using spent catalyst (1) produced from HDS of kerosene.
Conditions: pressure 60 bar, Time: 2 hrs Cat ./ feed: 2/10

Yield product W% / Temp.°C	Feed	350	375	400	425
HC. Gas		5.87	6.75	7.37	8
H_2S + NH_3 + Loss		0.23	0.55	0.83	.1
Total liquid yield wt.%		93.9	92.7	91.8	90.9
Naphtha (C_5-170°C)		0.5	1	1.5	2
Gas oil (170-350°C)		20.9	23	25.1	27.3
Vacuum gas oil (360-500°C)		26.4	28.2	30.1	32.4
Heavy oil 500+°C		46.1	40.5	35.1	29.2
Characteristics of heavy oil 500+°C					
Sulfur content wt %	4.63	1.67	1.45	1.3	1.02
Metal content ppm	303	63.59	51.47	39.36	24.22
C-carbon residue wt.%	18.75	5.25	4.31	3.38	2.44
HDS %		64	68	72	78
HDM %		79	83	87	92
C-carbon removal wt %		72	77	82	87

Table (3): Effect of Reaction temperature on hydroprocessing of vacuum Residue using spent catalyst (2) produced from HDS of gas oil. Conditions: pressure 60 bar, Time 2 hrs Cat ./ feed: 2/10

Yield product wt.% / Temp.°C	Feed	350	375	400	425
HC. Gas		2.44	3	4.95	6.1
H_2S + NH_3 + Loss		0.16	0.4	0.7	0.9
Total liquid yield wt.%		97.4	96.6	94.35	93
Naphtha (C_5-170°C)		0.4	0.6	0.85	1.2
Gas oil (170-350°C)		20.5	21.2	23	25
Vacuum gas oil (360-500°C)		27.3	30	34	36
Heavy oil 500+°C		49.2	44.8	36.5	30.8
Characteristics of heavy oil 500+°C					
Sulfur content wt%	4.63	1.85	1.67	1.48	1.3
Metal (N1+V) ppm	303	84.78	66.62	51.48	39.36
C-carbon residue wt.%	18.75	5.81	5.06	4.13	3.38
HDS %		60	64	68	72
HDM %		72	78	83	87
C-carbon removal %		69	73	78	82

Table (4): Effect of Reaction temperature on hydroprocessing of vacuum Residue using spent catalyst (3) produced from re-refining of waste oil. Conditions: pressure 60 bar, Time 2 hrs Cat ./ feed: 2/10

Yield Product wt.% / Temp.°C	Feed	350	375	400	425
HC. Gas		0.85	2.35	2.9	4.27
H_2S + NH_3 + Loss		0.05	0.3	0.5	0.73
Total liquid yield wt.%		99.1	97.35	96.6	95
Naphtha (C_5-170°C)		0.3	0.39	0.6	0.9
Gas oil (170-350°C)		18.3	20.1	22	24
Vacuum gas oil (360-500°C)		29.5	34	36	38
Heavy oil 500+°C		51	42.56	38	32.1
Characteristics of heavy oil 500+°C					
Sulfur content wt%	4.63	1.89	1.81	1.62	1.48
Metal (N1+V) ppm	303	105.98	90.84	75.7	60.56
C-carbon residue wt.%	18.75	7.5	6.19	5.25	4.13
HDS %		59	61	65	68
HDM %		65	70	75	80
C-carbon removal %		60	67	72	78

Table (5): Effect of catalyst/Feed ratio on hydroprocessing of vacuum Residue using spent catalyst (1)
Condition : Temp. 400C^{0} , pressure 60 bar , Time 2 hrs

Yield Product wt.% / Cat /feed	Feed	1/10	2/10	3/10
HC. Gas		5.87	7.37	8.55
$H_2S + NH_3 +$ Loss		0.23	0.83	1.4
Total liquid yield wt.%		93.9	91.8	92.05
Naphtha (C_5-170^{0}C)		0.5	1.5	2.75
Gas oil (170-350^{0}C)		22	25.1	27.1
Vacuum gas oil (360-500^{0}C)		27.5	30.1	32.9
Heavy oil 500^{0+}C		43.9	35.1	27.3
Characteristics of heavy oil 500^{0+}C				
Sulfur content wt%	4.63	1.57	1.3	0.97
Metal (Ni+v) ppm	303	54.5	39.36	24.22
C-carbon residue wt.%	18.75	4.5	3.38	2.25
HDS %		66	72	79
HDM %		82	87	92
C-carbon removal %		76	82	88

Table (6): Effect of catalyst /Feed ratio on hydroprocessing of vacuum Residue using spent catalyst (2)
Condition:- temperature 400^{0}C , pressure : 60 bar, Tim 2 hrs

Yield Product wt.% / Cat/Feed	Feed	1/10	2/10	3/10
HC. Gas		2.9	4.95	6.75
$H_2S + NH_3 +$ Loss		0.2	0.7	1.2
Total liquid yield wt.%		96.9	94.35	92.05
Naphtha(C_5-170^{0}C)		0.43	0.85	1.75
Gas oil (170-350^{0}C)		20	23	25.1
Vacuum gas oil (360-500^{0}C)		32.4	34	35.9
Heavy oil 500^{0+}C		44.07	36.5	29.3
Characteristics of heavy oil 500^{0+}C				
Sulfur content wt %	4.63	1.8	1.48	1.2
Metal (Ni+V) ppm	303	66.6	51.48	36.34
C-carbon residue wt.%	18.75	5.25	4.13	3.0
HDS %		62	68	75
HDM %		78	83	88
C-carbon removal %		72	78	84

Table (7): Effect of catalyst Feed ratio on hydroprocessing of vacuum Residue using spent catalyst (3)
Conditions : Temperature 400C°, pressure : 60 bar, Time 2 hrs

Yield Product wt.% Cat/Feed	Feed	1/10	2/10	3/10
HC. Gas		0.85	2.9	4.9
H_2S + NH_3 + Loss		0.1	0.5	1
Total liquid yield wt.%		99.05	96.6	94.1
Naphtha (C_5-170°C)		0.18	0.60	0.81
Gas oil (170-350°C)		20	22	23.9
Vacuum gas oil (360-500°C)		34.6	36	38
Heavy oil 500+°C		44.27	38	31.39
Characteristics of heavy oil 500+°C				
Sulfur content wt%	4.63	1.94	1.62	1.29
Metal cont ppm	303	90.84	75.7	60.56
C-carbon residue wt.%	18.75	6.19	5.25	4.13
HDS %		58	65	72
HDM %		70	75	80
C-carbon removal %		67	72	78

Table (8): Comparison between three spent catalysts during demetallation and deasphalting of vacuum residue at 400°C, 2 hrs, 60 bar and 2/1 cat./ feed ratio

Characteristics	Spent (1)	Spent (2)	Spent (3)
HC. Gas	7.37	4.95	2.9
H_2S + NH_3 + Loss	0.83	0.7	0.5
Total liquid yield wt.%	91.8	94.35	96.6
Naphtha (C_5-170°C)	1.5	0.85	0.6
Gas oil (170-350°C)	25.1	23	22
Vacuum gas oil (360-500°C)	30.1	34	36
Heavy oil 500+°C	35.1	36.5	38
Characteristics heavy oil 500+			
HDS %	72	68	65
HDM %	87	83	75
C-carbon removal %	82	78	72

Table (9): Effect of catalysts type on total sulphur content during hydroconversion of vacuum residue at 400°C, 2 hrs, 60 bar and 2/1 cat./ feed ratio

Characteristics	Spent (1)	Spent (2)	Spent (3)
Total liquid yield wt.%	1.53	1.99	2.25
Naphtha (C_5-170°C)	0.05	0.08	0.10
Gas oil (170-350°C)	0.10	0.19	0.25
Vacuum gas oil (360-500°C)	0.16	0.21	0.27
Heavy oil 500+°C	1.30	1.48	1.62

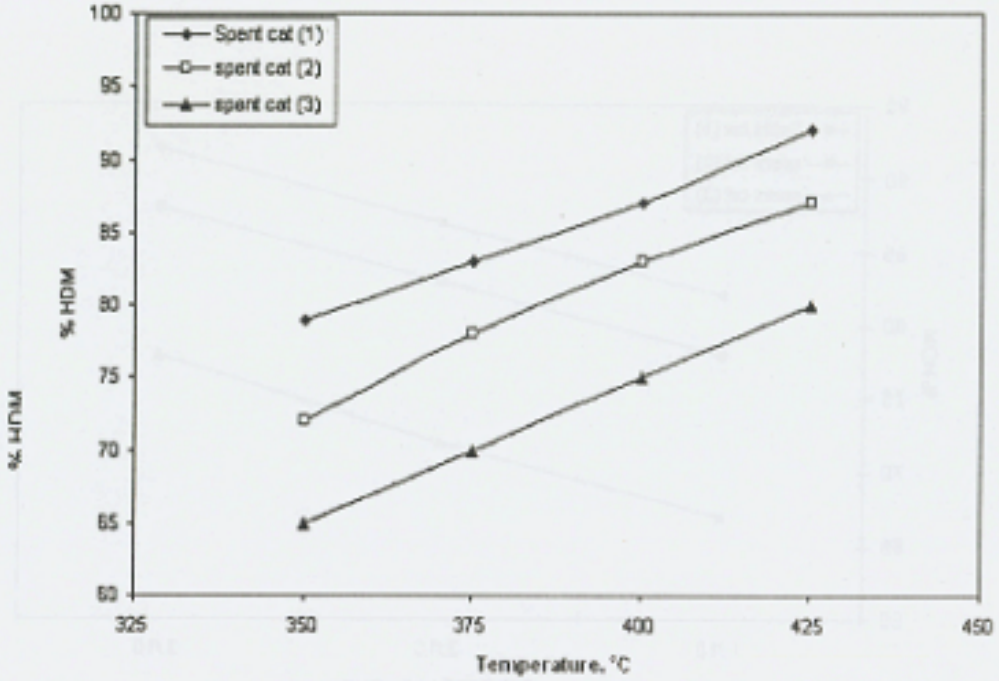

Fig. (1) effect of reaction temperature on HDM of Heavy vacuum Residue using different spent catalysts

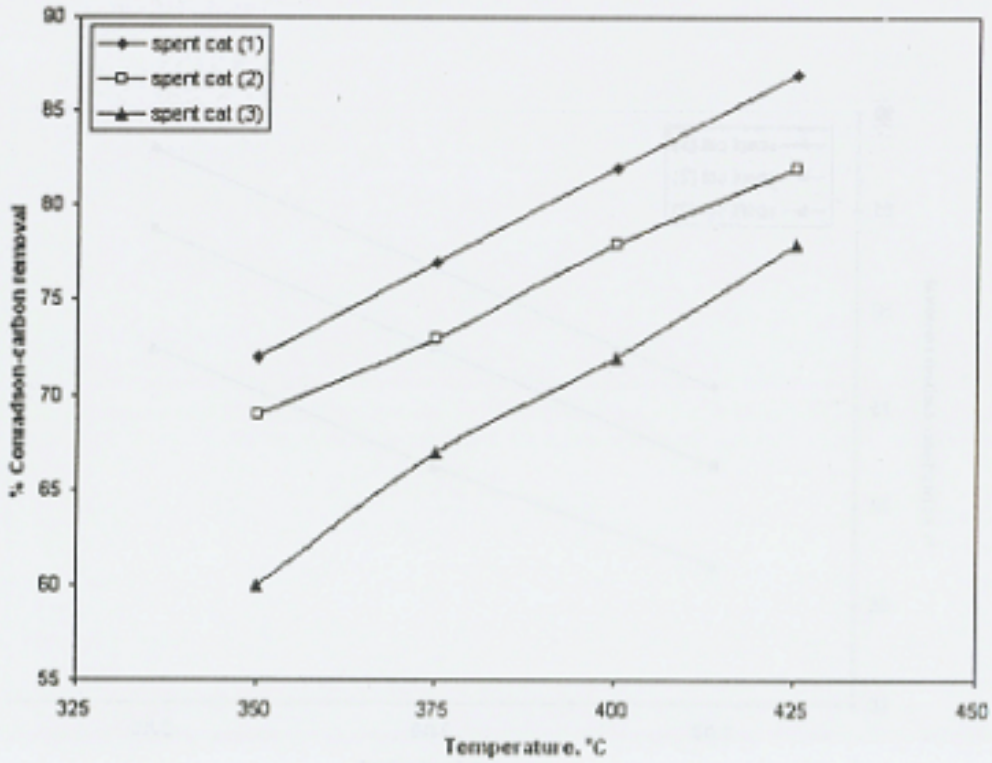

Fig. (2) Effect of temperature on conradson-carbon removal of heavy vacuum Residue using different spent catalysts

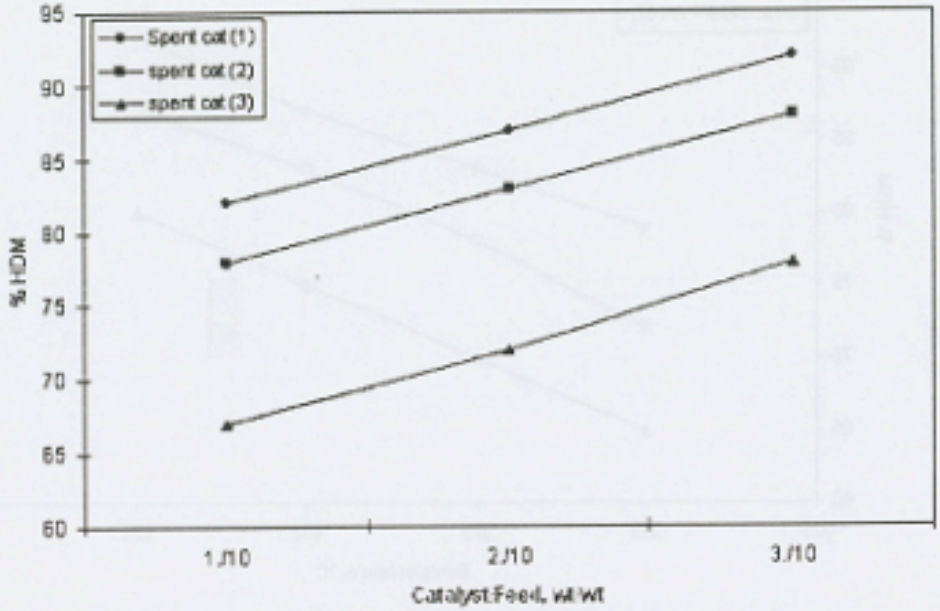

Fig.(3) Effect of catalyst/ Feed ratio on HDM of Heavy vacuum Residue using different spent catalyst

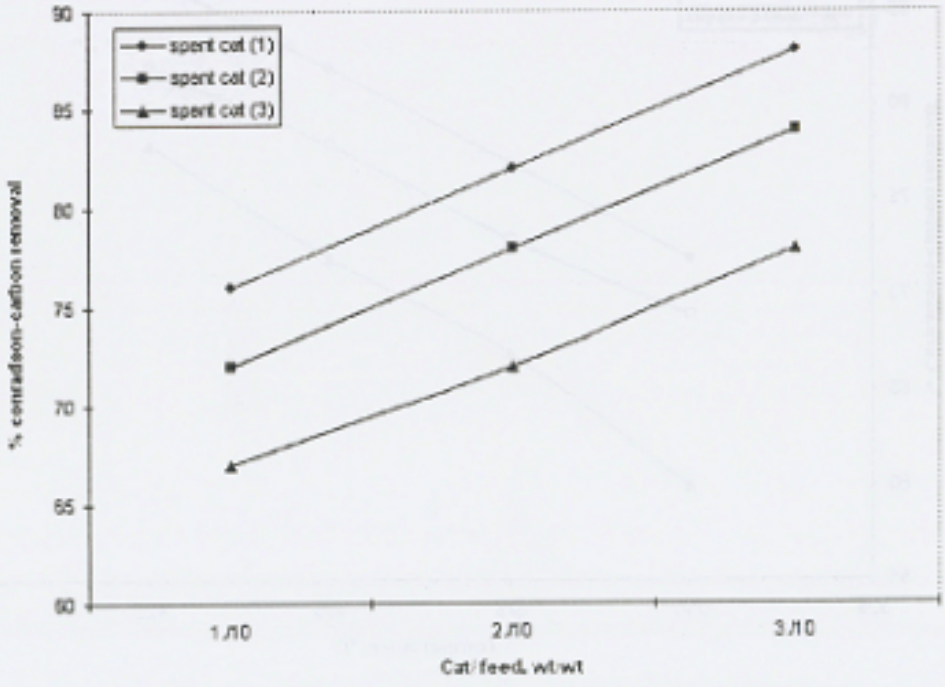

Fig. (4) Effect of catalyst Feed ratio on conradsen carbon removal of Heavy vacuum Residue using different spent catalyst

CONCLUSION

Powder catalysts act as a site for the deposition of metals ,coke and reduced this impurities from vacuum heavy residue.

Hydrodemetallation (HDM) activities for the three spent catalysts were higher than that for the hydrodesulphurization (HDS) activities.

, hydrodemetallation (HDM) and conradson carbon removal for spent catalyst (1) produced from hydrodesulphurization of kerosene was higher than that of other catalysts.

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دراسة على ازالة المعادن والأسعلتينات من المتخلف البترولى الثقيل : الجزء الثانى

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معهد بحوث البترول حى الزهور -مدينة نصر - القاهرة

أستكمالاً للدراسة فى الجزء الأول قد تناولت هذه الدراسة طرق معالجة المتخلف البترولى الثقيل عن طريق عمليات الهدرجة لازالة المعادن والكبريت باستخدام الحفازات السابق استعمالها فى عمليات التكرير المختلفة بدل من الحفازات الجديدة وهذه الحفازات هى :

الحفاز الأول ناتج من عمليات الهدرجة للنفط وقد سبق استعماله فى وحدة الهدرجة لمدة عشر سنوات

الحفاز الثانى ناتج من عمليات الهدرجة للسولار وقد سبق استعماله فى وحدة الهدرجة لمدة عشر سنوات

الحفاز الثالث وقد سبق استخدامه فى عمليات استرجاع زيوت التزيت لمدة خمس سنوات

وبدراسة ظروف التشغيل المختلفة لهذه الحفازات من حراره ونسبه تعديه الى الحفاز فى جهاز الأوتوكلايف قد أظهرت النتائج ان الحفاز المستعمل من عمليات هدرجة النفط عند ظروف تشغيل درجة حراره ٤٠٠م وضغط ٦٠ بار ونسبه حفاز الى التغذيه ١٠/٢ قد أدى الى تحسن فى خواص الزيت الناتج من حيث ازالة المعادن والمواد الكبريتيه

وقد خلصت هذه الدراسه الى ما يلى : نجاح استخدام الحفازات المستعمله وخصوصا المستخدمه فى عمليه الهدرجة للنفط فى عمليات ازالة الأسعلت وتخفيض نسبة المعادن والمواد الكبريتيه من المتبقى البترولى الثقيل